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(54) A process for the preparation of ferrierite, ferrierite thus obtained and its use as catalyst or catalyst carrier for converting hydrocarbons, and for separating hydrocarbons.

(57) A process for the preparation of ferrierite by heating at a temperature between 100 and 200° C an aqueous mixture which contains a compound of an alkali metal (M), a compound of aluminium, a compound of silicon, and piperidine and/or alkylsubstituted piperidine (NR), in which aqueous mixture the various compounds are present in the following molar ratios, which except for piperidine and alkyl-substituted piperidine, are expressed in moles of the oxides:

SiO_2: $Al_2O_3 > 15$;
H_2O: $SiO_2 = 5$–500;
NR: $SiO_2 = 0.05$–1.0, and
M_2O: $Al_2O_3 > 1$.

Ferrierite thus obtained and its use as catalyst or catalyst carrier for converting hydrocarbons and as molecular sieve, for instance for separating hydrocarbons.

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A PROCESS FOR THE PREPARATION OF FERRIERITE, FERRIERITE THUS OBTAINED AND ITS USE AS CATALYST OR CATALYST CARRIER FOR CONVERTING HYDROCARBONS, AND FOR SEPARATING HYDROCARBONS

The invention relates to a process for the preparation of ferrierite.

Ferrierite is a crystalline aluminosilicate zeolite, which is used, inter alia, as adsorbent and as catalyst or catalyst carrier. Ferrierite can be prepared by maintaining an aqueous mixture containing one or more alkali metal compounds, one or more aluminium compounds and one or more silicon compounds in a given ratio at elevated temperature until the ferrierite has been formed and subsequently separating the ferrierite crystals from the mother liquor. This procedure has three drawbacks, which are connected with the reaction temperature and with the purity and the molar SiO_2/Al_2O_3 ratio of the ferrierite. As regards the reaction temperature it has been found that this procedure requires temperatures higher than 300°C. These high reaction temperatures involve the use of high pressures, which necessitates the use of expensive high-pressure equipment. As regards the molar SiO_2/Al_2O_3 ratio of the ferrierite it has been found that this procedure produces as a rule ferrierite with a molar SiO_2/Al_2O_3 ratio lower than 15. When the ferrierite is used for catalytic purposes, a ferrierite with a higher molar SiO_2/Al_2O_3 ratio is needed in view of the catalyst stability. In the above-mentioned procedure the purity of the ferrierite also leaves much to be desired. As a rule a solid product is obtained consisting of less than 80%w ferrierite.

The Applicant has done an investigation concerning the preparation of ferrierite. In this investigation a procedure was found which provides a considerable improvement in connection with each of the three above-mentioned drawbacks. In this procedure the starting material is, as usual, an aqueous mixture containing one or more compounds of an alkali metal (M), one or more aluminium compounds and one or more silicon compounds. In addition, piperidine and/or one or more alkyl-substituted

piperidines (NR) are incorporated into the aqueous mixture. The amounts of the various compounds in the aqueous mixture should be chosen such that the following requirements with respect to molar ratios, which except for piperidine and alkyl-substituted piperidines, are expressed in moles of the oxides, are satisfied:

$SiO_2 : Al_2O_3 > 15$,
$H_2O : SiO_2 = 5\text{-}500$,
$NR : SiO_2 = 0.05\text{-}1.0$, and
$M_2O : Al_2O_3 > 1$

A solid product consisting of more than 90%w ferrierite is formed by heating the aqueous mixture at a temperature between 100 and 200°C. The ferrierite has a molar SiO_2/Al_2O_3 ratio higher than 20.

The present patent application therefore relates to a process for the preparation of ferrierite by maintaining an aqueous mixture which contains one or more compounds of an alkali metal (M), one or more aluminium compounds and one or more silicon compounds at elevated temperature until the ferrierite has been formed and subsequently separating the ferrierite crystals from the mother liquor, which process is characterized in that

(a) the mixture contains piperidine and/or one or more alkyl-substituted piperidines (NR);

(b) in the mixture the various compounds are present in the following molar ratios, which except for piperidine and alkyl-substituted piperidines, are expressed in moles of the oxides:

$SiO_2 : Al_2O_3 > 15$,
$H_2O : SiO_2 = 5\text{-}500$,
$NR : SiO_2 = 0.05\text{-}1.0$, and
$M_2O : Al_2O_3 > 1$;

(c) the preparation of ferrierite is effected by heating the mixture at a temperature between 100 and 200°C.

In the preparation of ferrierite according to the invention it is essential that the aqueous mixture that is used as the starting material contains piperidine and/or one or more alkyl-substituted piperidines. As regards the required presence of piperidine and/or alkyl-substituted piperidines in the aqueous mixture it has been found that, if in this mixture the compounds mentioned are replaced by closely related heterocyclic nitrogen compounds such as pyrrole, imidazole, pyridine or pyrrolidone, either no ferrierite is formed at all, or the ferrierite obtained is highly contaminated with other zeolitic and/or amorphous material.

If the use of an alkyl-substituted piperidine is desired in the preparation of ferrierite according to the invention, alkyl piperidines containing only one alkyl substituent as well as alkyl piperidines containing two or more alkyl substituents are eligible for this purpose. If the alkyl piperidines contain only one alkyl substituent, this alkyl substituent may be present either at the nitrogen atom or at one of the carbon atoms of the piperidine. Examples of suitable monoalkyl piperidines in which the alkyl substituent is bonded to a carbon atom of the piperidine are 2-methyl, 3-methyl, 4-methyl, 2-ethyl, 3-ethyl and 2-propyl piperidine. Examples of suitable monoalkyl piperidines in which the alkyl substituent is bonded to the nitrogen atom of the piperidine are: 1-methyl, 1-ethyl, 1-propyl, 1-butyl, 1-pentyl, 1-octyl and 1-dodecyl piperidine. If it is desired in the preparation of ferrierite according to the invention to use an alkyl-substituted piperidine containing two or more alkyl substituents, suitable alkyl piperidines for this purpose are those in which all alkyl substituents are present at carbon atoms of the piperidine as well as those in which one of the alkyl substituents is present at the nitrogen atom of the piperidine and the rest of the alkyl substituents at carbon atoms of the piperidine. An example of a suitable alkyl-substituted piperidine of the latter group is 1,2-dimethyl piperidine. If the ferrierite preparation according to the invention is carried out using an

alkyl-substituted piperidine,it is preferred to use a methyl piperidine for this purpose. As alkali metal, silicon and aluminium compounds which are to be incorporated into the aqueous mixture from which ferrierite is prepared according to the invention, in principle, all such compounds as have been used in the past in the preparation of this zeolite, are suitable. The alkali metal compound that is preferably used is a sodium compound. For the silicon compound and the aluminium compound preference is given to sodium water glass and aluminium sulphate.

As regards the amounts of the various components in the aqueous mixture from which ferrierite is prepared according to the invention it is preferable that these components are present in the following molar ratios, which except for piperidine and alkyl-substituted piperidines are expressed in moles of the oxides:

$SiO_2 : Al_2O_3 > 20$,
$H_2O : SiO_2 = 10\text{-}100$, and
$NR : SiO_2 = 0.2\text{-}0.6$

Ferrierite is a zeolite of the molecular sieve type whose accessibility is determined by pores having a diameter of about 0.6 nm. Ferrierite is very suitable as catalyst or catalyst carrier in a variety of catalytic processes. In view of the uniform pore diameter of ferrierite, this material is especially important for selectively carrying out catalytic processes in which either from a mixture of compounds with linear and branched structures substantially the compounds with linear structure are to be converted, or from a certain compound substantially compounds with linear structure are to be formed. Examples of such catalytic processes are selective (hydro)cracking and dehydrogenation of n-paraffins. When ferrierite is used as a catalyst or catalyst carrier, preference is given to a material whose alkali metal content has been reduced to less than 1%w and in particular to less than 0.05%w. Reducing the alkali metal content of ferrierite can conveniently be carried out by contacting the ferrierite

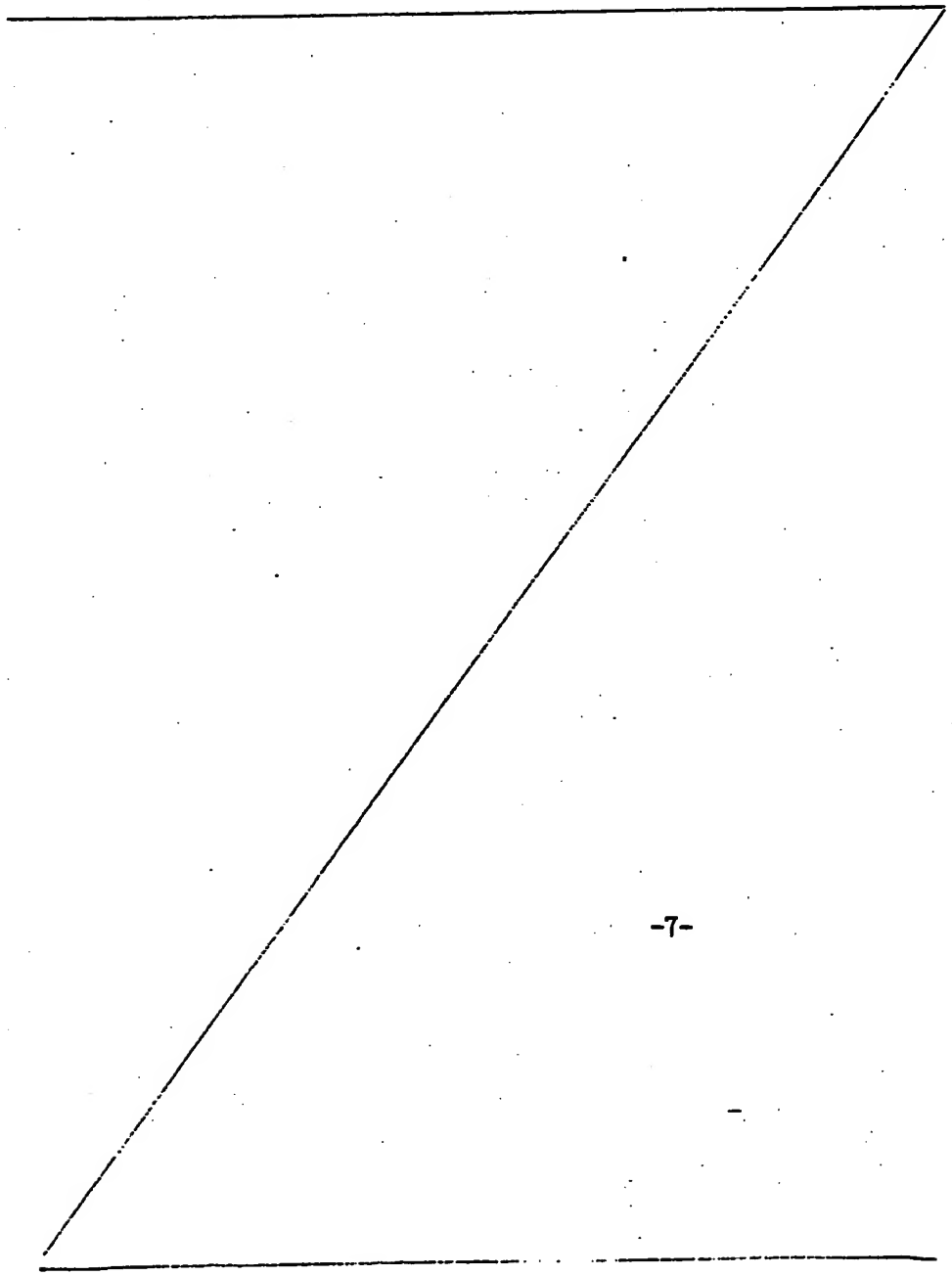
once or several times with a solution containing ammonium ions and calcining the NH_4^+ ferrierite thus obtained, which yields the H^+ ferrierite. When ferrierite is used for catalytic purposes, it is preferably employed as carrier material for one or more catalytically active metal components. Ferrierite is very suitable for use as catalyst carrier in hydrocarbon conversion processes such as cracking, isomerization, dealkylation and hydrocracking. To this end one or more active metal components which impart hydrogenation-dehydrogenation properties to the ready catalyst are deposited on the ferrierite. Very suitable for this purpose are one or more metals of Groups VIB, VIIB and VIII of the Periodic Table. The ferrierite-based catalysts are especially important for converting hydrocarbons by hydrocracking. As a result of the uniform pore diameter of ferrierite these catalysts are pre-eminently suitable for selectively hydrocracking substantially n-paraffins in hydrocarbon oils consisting of mixtures of n-paraffins and other hydrocarbons (catalytic dewaxing).

In addition to the use of ferrierite as the carrier for catalysts for converting hydrocarbons, an important application of this material is as a molecular sieve for separating compounds with a substantially unbranched structure from mixtures of these compounds with related compounds with branched and/or cyclic structure. For this application the ferrierite should be at least partially dehydrated.

The invention will now be illustrated by the following Examples. In all examples the following procedure was used. An organic nitrogen compound was incorporated with stirring into a solution of sodium water glass (28%w SiO_2; 8%w Na_2O) in water. To the mixture thus obtained a solution of aluminium sulphate in water or in a mixture of water and sulphuric acid was added with stirring. The resultant mixture was stirred for a further 15 minutes and then maintained for a certain time at a temperature of 150°C. The solid product was isolated from the reaction mixture.

The composition of the starting mixtures, the reaction time used, the composition of the isolated product and the molar SiO_2/Al_2O_3 ratio of the ferrierite are given in the Table below.

Examples 1-9 in the Table are according to the invention; Examples 10-13 have been included for comparison.



Example No.	Molar composition of the starting mixture	Reaction time, h	Composition of the isolated solid product, %w	Molar SiO_2/Al_2O_3 ratio of the ferrierite
1	93.5 SiO_2. 0.5 Al_2O_3. 21.4 Na_2O. 5.6 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	40
2	93.5 SiO_2. Al_2O_3. 10 Na_2O. 17 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	48
3	93.5 SiO_2. Al_2O_3. 21.4 Na_2O. 5.6 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	30
4	93.5 SiO_2. Al_2O_3. 24 Na_2O. 3 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	27
5	60 SiO_2. Al_2O_3. 2.7 Na_2O. 14.6 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	69
6	60 SiO_2. Al_2O_3. 6.6 Na_2O. 10.7 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	47
7	93.5 SiO_2. 2 Al_2O_3. 10 Na_2O. 17 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	34
8	93.5 SiO_2. 2 Al_2O_3. 17.7 Na_2O. 9.3 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	25
9	93.5 SiO_2. 4 Al_2O_3. 10 Na_2O. 17 Na_2SO_4. 36.7 piperidine. 1938 H_2O	113	Ferrierite : 100	22
10	93.5 SiO_2. Al_2O_3. 7.4 Na_2O. 19.6 Na_2SO_4. 36.7 pyrrole. 1938 H_2O	140	Ferrierite : 50 Amorphous material : 50	
11	93.5 SiO_2. Al_2O_3. 7.4 Na_2O. 19.6 Na_2SO_4. 36.7 imidazole. 1938 H_2O	140	Ferrierite : 0 Other zeolitic material : 80 Amorphous material : 20	

Example No.	Molar composition of the starting mixture	Reaction time, h	Composition of the isolated solid product, %w	Molar SiO_2/Al_2O_3 ratio of the ferrierite
12	93.5 SiO_2. Al_2O_3. 7.4 Na_2O. 19.6 Na_2SO_4. 36.7 pyridine. 1938 H_2O	140	Ferrierite : 50 Other zeolitic material : 30 Amorphous material : 20	
13	93.5 SiO_2. Al_2O_3. 7.4 Na_2O. 19.6 Na_2SO_4. 36.7 pyrrolidone. 1938 H_2O	140	Ferrierite : 30 Other zeolitic material - alpha-quartz : 50 Amorphous material : 20	

CLAIMS

1. A process for the preparation of ferrierite by maintaining an aqueous mixture which contains one or more compounds of an alkali metal (M), one or more aluminium compounds and one or more silicon compounds at elevated temperature until the ferrierite has been formed and subsequently separating the ferrierite crystals from the mother liquor, characterized in that:

(a) the mixture contains piperidine and/or one or more alkyl-substituted piperidines (NR);

(b) in the mixture the various compounds are present in the following molar ratios, which except for piperidine and alkyl-substituted piperidines, are expressed in moles of the oxides:

$SiO_2 : Al_2O_3 > 15$;

$H_2O : SiO_2 = 5\text{-}500$;

$NR : SiO_2 = 0.05\text{-}1.0$, and

$M_2O : Al_2O_3 > 1$;

(c) the preparation of ferrierite is effected by heating the mixture at a temperature between 100 and 200°C.

2. A process according to claim 1, characterized in that a methyl piperidine is used as alkyl-substituted piperidine.

3. A process according to claim 1 or 2, characterized in that a sodium compound is used as alkali metal compound.

4. A process according to any one of claims 1-3, characterized in that sodium water glass is used as silicon compound and aluminium sulphate as aluminium compound.

5. A process according to any one of claims 1-4, characterized in that in the aqueous mixture the various compounds are present in the following molar ratios, which except for piperidine and alkyl-substituted piperidines, are expressed in moles of the oxides:

$SiO_2 : Al_2O_3 > 20$;
$H_2O : SiO_2 = 10-100$, and
$NR : SiO_2 = 0.2-0.6$.

6. A process for the preparation of ferrierite, substantially as described and with special reference to Examples 1-9.

7. Ferrierite, characterized in that it has been prepared according to a process as claimed in claim 6.

8. Catalysts, characterized in that they contain one or more metals of Groups VIB, VIIB and VIII on a ferrierite according to claim 7 as the carrier, of which ferrierite the alkali metal content has been reduced to less than 0.05%w.

9. Molecular sieves, characterized in that they consist of a ferrierite according to claim 7, which has at least partly been dehydrated.

10. A process for converting hydrocarbons, in particular the selective hydrocracking of substantially n-paraffins in mixtures of n-paraffins with other hydrocarbons, characterized in that a catalyst according to claim 8 is used.

11. A process for separating compounds with a substantially unbranched structure from mixtures of these compounds with related compounds with branched and/or cyclic structure, characterized in that a molecular sieve according to claim 9 is used.

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EUROPEAN SEARCH REPORT

0012473
Application number
EP 79 20 0717

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 000 248 (D.E. MARTIN) & DE - A - 2 507 426 FR - A - 2 264 777 --	
A	FR - A - 2 228 721 (MOBIL OIL CORP.) * Page 3, lines 3-5 * --	
A	US - A - 4 016 245 (C.J. PLANK et al.) * Column 2, lines 55-61 * --	
A	US - A - 4 046 859 (C.J. PLANK et al.) * Column 3, lines 42-50 * --	
A	US - A - 3 933 974 (B.H.C. WINQUIST) & DE - A - 2 606 097 FR - A - 2 301 479 --	
A	DE - A - 2 817 577 (MOBIL OIL CORP.) * Page 21, last line, 1st paragraph * & BE - A - 866 272 --	
A	ZEITSCHRIFT FUR CHEMIE, vol. 13, 1973, no. 3, Leipzig DE F. WOLF et al. "Uber den Einfluss	

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CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)

C 01 B 33/28
B 01 J 29/28
20/18
C 10 G 45/64
25/03

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 01 B 33/28

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	07-03-1980	BREBION

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EUROPEAN SEARCH REPORT

Application number 0012473

EP 79 . . 0717

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	organischer Verbindungen auf die hydrothermale Synthese zeolithischer Molekularsiebe der Typen A,X, und Y", pages 109-110 * Page 109, right-hand column, last but one whole paragraph * ----		TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

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